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Crystal Structure-Selective Formation and Carrier Dynamics of Type-II CdS–$Cu_{31}S_{16}$ Heterodimers

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Anisotropically phase-segregated CdS–$Cu_{31}S_{16}$ heterodimers with type-II band alignment were spontaneously formed by selective growth of monoclinic $Cu_{31}S_{16}$ phases on preformed hexagonal CdS phases. The photo-induced carrier dynamics of the heterodimer was investigated by fluorescence and transient absorption measurements.

The primary structures such as size and shape of inorganic nanoparticles (NPs) determine their physical and chemical properties. Control of their structures is required for both the elucidation of structure-dependent properties and the directed assembly of hierarchical structures.[1-10] NPs synthesized from two distinct chemical species are generally chemically disordered alloys or core–shell structures, in which the two chemical species are isotropically distributed. The distribution of these chemical species is another determinant of the NPs' properties and function. Recently, anisotropically two phase-segregated NPs, heterodimers, have received much attention[11,12] because they are expected to provide new ways to manipulate wave functions,[13,14] plasmon resonances[15] and spin.[16] They can not only exhibit multiple functions, but also realize charge-separation at the heterointerface. For example, there have been many reports on heterostructured NPs synthesized with combinations of semiconductor–metals and semiconductor–semiconductors. The semiconductor-metal combinations, such as CdSe–Au,[17,18] CdSe–Pt[19] and PbS–Au,[20] provide photoexcited charge transfer from the semiconductor to the metal phase. Semiconductor–semiconductor combinations, such as CdS–CdSe,[21,22] CdSe–CdTe,[23-25] CdS–ZnSe[26] and CdS–CdTe,[27] can enhance quantum yields or provide efficient spatial charge separation, depending on the band alignment.

Among three types of heterojunctions of semiconductor–semiconductor heterodimers, type-II band alignment is requisite to the photoexcited charge separation. The combination of CdS with Cu_2S has been vigorously studied more than 50 years ago, where the Cu_2S phase with a band gap of 1.21 eV absorbs almost all the solar energy and the photoexcited electrons are transferred into the conduction band of the CdS phase.[28] CdS–Cu_2S heterodimers are promising materials, which can enhance the performance and reduce the manufacturing cost performance of NP-based solar cells. Recently, Alivisatos and co-workers applied the cation exchange reaction to the fabrication of a dense array of perpendicularly aligned CdS–Cu_2S heterodimer nanorods for high performance photoelectric conversion device.[29] Han and co-workers also demonstrated ultrafast charge separation in CdS–$Cu_{1.94}S$ nanodisks.[30] It should be noted that, for the Cu_2S-cotaining heterodimers, an oxidative self-doping of Cu_2S has a potential drawback. The formation of nonstoichiometric $Cu_{2-x}S$ ($x > 0$) NPs from the Cu_2S NPs by oxidation at ambient atmosphere exhibited a vacancy-induced quenching.[31] An investigation of the effect of copper vacancies on the photo-induced carrier dynamics of the CdS–$Cu_{2-x}S$ ($x > 0$) heterodimers is an important issue for the practical application of the $Cu_{2-x}S$-containing semiconductor–semiconductor heterodimers.

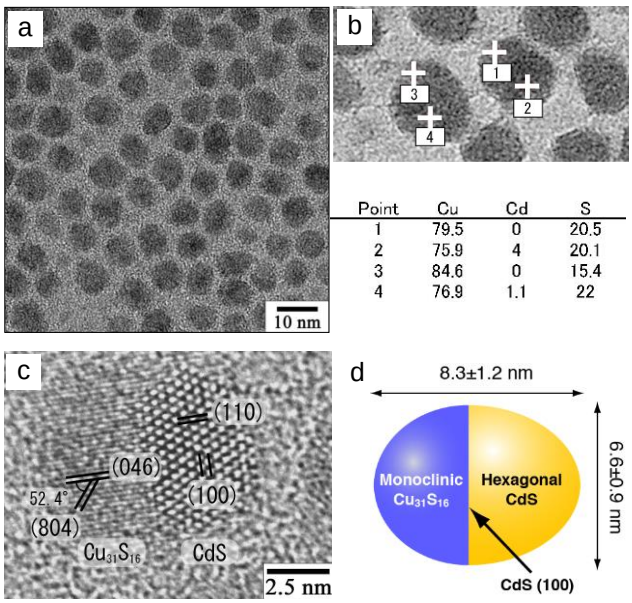

Fig. 1 (a) TEM image, (b) nano-spot EDX results, (c) HRTEM image and (d) schematic of the CdS–$Cu_{31}S_{16}$ heterodimer.

Here, we report the unique formation of CdS–$Cu_{31}S_{16}$ heterodimers by the in-situ seeded growth of the $Cu_{31}S_{16}$ phase selectively on preformed hexagonal CdS NPs, as observed in the PdS_x–Co_9S_8 system.[32,33] In addition, the carrier dynamics of both the CdS–$Cu_{31}S_{16}$ heterodimers and $Cu_{31}S_{16}$ NPs are investigated by means of the fluorescence and transient absorption measurement. The role of copper vacancies in $Cu_{2-x}S$ played in the photo-induced carrier dynamics is discussed.

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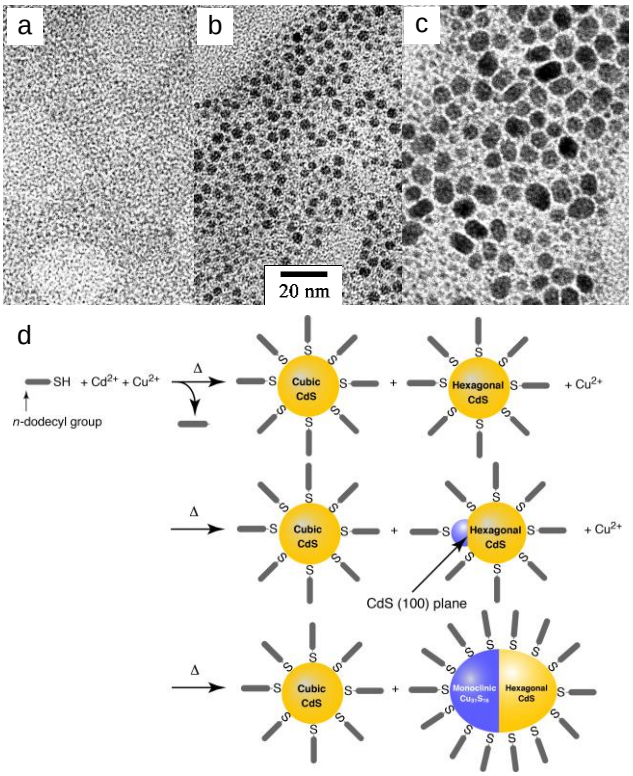

Fig. 2 TEM images of the CdS–$Cu_{31}S_{16}$ heterodimers synthesized with reaction times of (a) 20 min, (b) 30 min and (c) 60 min. (d) Speculated formation mechanism of the CdS–$Cu_{31}S_{16}$ heterodimers.

The CdS–$Cu_{31}S_{16}$ heterodimers were synthesized in a one-pot reaction. The reaction mixture of $Cd(acac)_2$ (0.50 mmol), $Cu(acac)_2$ (0.50 mmol), 1,2-hexadecanediol and 1-dodecanethiol (6.0 mmol), which provided surface passivation and acted as a sulfur source, in di-*n*-octylether (10 mL) was heated at 240 °C for 60 min under nitrogen. Centrifugal purification with ethanol/hexane afforded CdS–$Cu_{31}S_{16}$ heterodimers as precipitates. Figure 1a shows a transmission electron microscopy (TEM) image of the resulting CdS–$Cu_{2-x}S$ heterodimers. The relatively small difference in electron transmittance properties between CdS and $Cu_{2-x}S$ phases means these heterodimers look like single phase particles. However, local chemical composition analysis of a single heterodimer measured by nano-spot energy-dispersive X-ray (EDX) spectroscopy showed that the heterodimers were composed of Cd-rich and Cu-rich phases (Fig. 1b). This is a strong indication of anisotropic phase-segregation of the CdS and $Cu_{2-x}S$ phases. It should be noted that an excess amount of copper was observed for all samples, because the EDX measurements were carried out on amorphous carbon-coated copper grids (Elemental copper was also detected from a TEM grid without heterodimers). Further analysis by high resolution TEM (HRTEM) (Fig. 1c) clearly demonstrated that the phase-segregated CdS–$Cu_{31}S_{16}$ heterodimer consists of hexagonal CdS (right phase) and monoclinic $Cu_{31}S_{16}$ (left phase) phases. The CdS–$Cu_{31}S_{16}$ heterodimers were 8.3±1.2 nm long and 6.6±0.9 nm wide (Fig. 1d). The interfacial lattice plane was determined to be hexagonal CdS (100) plane. The HRTEM image also reveals that the (110) planes of the hexagonal CdS phases are aligned parallel to the (046) planes of the monoclinic $Cu_{31}S_{16}$ phases, both of which are perpendicular to the heterointerfaces (Fig. S1). According to this observation, the lattice mismatch was estimated to be 4.8 %, which is reasonable for heterojunction interface formation in the nanoscale crystals. Recent studies revealed the formation of heterostructured semiconductor NPs with large lattice mismatch and no dislocation. For example, CdTe NPs were epitaxially grown on the tips of CdSe nanorods with 7.1 % lattice mismatch to form dumbbell-shaped heterostructures.[23-25] In addition, heteroepitaxial growth of ZnSe shell on a CdTe NP core with 14.4 % lattice mismatch was also reported.[13,34] An excitonic Bohr radius for the well-studied CdS is 3 nm, while that for $Cu_{2-x}S$ is calculated to be about 3–5 nm if one assumes that the relative dielectric constant for copper sulfides is about 10–15.[35] Considering these Bohr radii, it is reasonable to think that the resulting CdS–$Cu_{31}S_{16}$ heterodimers, in which two distinct phases have the similar size, possess type-II band alignment.

TEM measurements were used to monitor the time evolution of the CdS–$Cu_{31}S_{16}$ heterodimer growth (Fig. 2a–c). After 20 min, small (approximately 2 nm) NPs were observed. Further reaction for 10 min gave a bimodal distribution of two different sized NPs. After 60 min, this size-difference was enhanced and small NPs and CdS–$Cu_{31}S_{16}$ heterodimers formed. Careful centrifugal purification with a controlled amount of ethanol was used to separate the small NPs remaining in the supernatant and CdS–$Cu_{31}S_{16}$ heterodimers as precipitates (Fig. S2a and b). The Cd/Cu molar ratios of NPs in the supernatant and precipitates determined by X-ray fluorescence analysis were 75/25 and 32/68, respectively. On XRD analysis, the NPs in the precipitate showed diffraction patterns of both hexagonal CdS and monoclinic $Cu_{31}S_{16}$ phases, whereas the diffraction pattern of the small NPs in the supernatant was assigned to pure cubic CdS phase (Figs. S2c, S2d, S3c and S3d for details). These results strongly suggest the CdS–$Cu_{31}S_{16}$ heterodimers have the following formation mechanism. First, the cubic and hexagonal CdS NPs are formed in the reaction solution. The monoclinic $Cu_{31}S_{16}$ phases then grow only on the hexagonal CdS NPs to form CdS–$Cu_{31}S_{16}$ heterodimers (Fig. 2d). In a typical seeded growth of heterostructured NPs, the second species epitaxially grows on the surface of the seed-NPs so as to minimize the interfacial free energy.[36,37] If there is no such interface between the two different phases, an isolated nucleation of the second species takes place.[38] In this case, the hexagonal CdS NPs acted as a growth substrate for the monoclinic $Cu_{31}S_{16}$ phases because the hexagonal CdS (100) planes can form stable interfaces with the monoclinic $Cu_{31}S_{16}$ phases. Consequently, the CdS–$Cu_{31}S_{16}$ heterodimers were formed through a seeded growth process on preformed hexagonal CdS phases. At present, the reason why the copper sulfide phase formed on the CdS NP is not Cu_2S but $Cu_{31}S_{16}$ remains unclear except for small lattice mismatch. This seeded growth process can be easily applied to obtain another CdS–copper sulfide heterostructures with the copper sulfide phases attached on different hexagonal CdS planes. According to the literature, hexagonal CdS nanowires were synthesized as seed nanosturctures, whose side walls ({100} and {010} planes) were strongly passivated by phosphonic acid.[39] Heating of the reaction mixture of CdS nanowires (10 mg), $Cu(acac)_2$ (0.05 mmol) and 1-dodecanethiol (0.3 mmol) in di-*n*-octylether (5 mL) at 210 °C for 60 min under nitrogen resulted in formation of phase-segregated CdS–copper sulfide nanowires (Fig. S4). The copper sulfide

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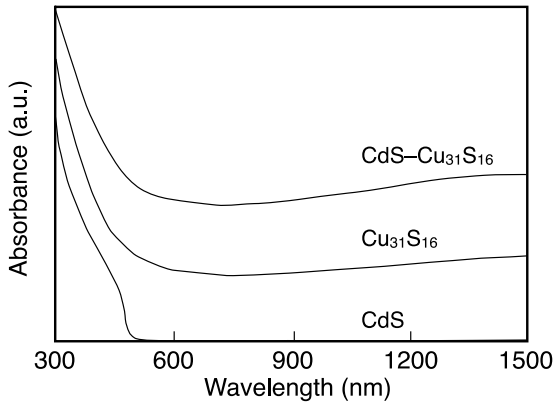

Fig. 3 UV-Vis-NIR absorption spectra of the CdS NPs, $Cu_{31}S_{16}$ NPs and CdS–$Cu_{31}S_{16}$ heterodimers.

phases selectively grew on the terminal positions ((001) planes) of the CdS nanowires, which have higher surface free energy than the side walls of the hexagonal CdS nanowires strongly passivated by phosphonic acid.

Finally, the optical properties of the CdS–$Cu_{31}S_{16}$ heterodimers were measured by ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectroscopy, photoluminescence (PL) spectroscopy and transient absorption measurement. Figure 3 shows UV-Vis-NIR spectra of the CdS–$Cu_{31}S_{16}$ heterodimers, 5.0 nm monoclinic $Cu_{31}S_{16}$ and 5.4 nm hexagonal CdS NPs (Fig. S3). The UV-Vis-NIR spectrum of the CdS–$Cu_{31}S_{16}$ heterodimers exhibited a simple superimposed spectrum of the monoclinic $Cu_{31}S_{16}$ and hexagonal CdS NPs. The CdS–$Cu_{31}S_{16}$ heterodimers had an absorption band at high energy (<700 nm), which is derived from an interband transition of CdS and $Cu_{31}S_{16}$ phases. The NIR absorption band at >800 nm is known to be ascribed to localized surface plasmon resonance of the vacancy-doped $Cu_{31}S_{16}$ NPs because copper defects in Cu_2S create free carriers (positive holes).[31,40] It is noteworthy that the $Cu_{1.94}S$ or CdS–$Cu_{1.94}S$ nanodisks with the same crystal structure did not showed the clear localized surface plasmon band,[31] inferring that the copper vacancies are introduced more efficiently in the $Cu_{31}S_{16}$ NPs owing to the difference in surfactant and/or exposed facet.[40] Moreover, this fact implies that the number of copper vacancies in CdS–$Cu_{31}S_{16}$ heterodimers is larger than that in previously reported CdS–$Cu_{1.94}S$ nanodisks.[30] The PL of the CdS or $Cu_{31}S_{16}$ phase in the CdS–$Cu_{31}S_{16}$ heterodimers was not observed, which probably indicates that efficient electron or energy transfer proceeds between the CdS and $Cu_{31}S_{16}$.

For better understanding of photo-induced carrier dynamics, we measured the exciton lifetimes of $Cu_{31}S_{16}$ NPs and CdS–$Cu_{31}S_{16}$ heterodimers by the transient absorption measurement using the fs-laser flash photolysis (see Fig. S5). The exciton lifetime of the $Cu_{31}S_{16}$ NPs (0.4 ± 0.1 ps) was significantly short compared with the previously reported value for the $Cu_{1.94}S$ nanodisks and the Cu_2S NPs (see S.I. for details).[30] The photogenerated exciton in $Cu_{31}S_{16}$ NPs is quickly consumed through the Auger type charge recombination and/or energy transfer to localized surface plasmon.[31] The exciton lifetime of the $Cu_{31}S_{16}$ phase in CdS–$Cu_{31}S_{16}$ heterodimer was similar to that of the $Cu_{31}S_{16}$ NPs (0.3 ± 0.1 ps, see S.I.), indicating that the photogenerated excitons were dominantly consumed via vacancy-induced decay processes (*i.e.*, Auger type charge recombination and/or energy transfer to localized surface plasmon) in the identical $Cu_{31}S_{16}$ phase rather than the electron transfer to the CdS phases.

Considering that the CdS–$Cu_{1.94}S$ nanodisks exhibited an electron transfer from $Cu_{1.94}S$ to CdS, it is a quite interesting and important feature that slightly more copper vacancies in the $Cu_{31}S_{16}$ phase of heterodimer suppressed the electron transfer from $Cu_{31}S_{16}$ to CdS. A theoretical calculation indicates that band structure of $Cu_{2-x}S$ ($x > 0$) should not significantly change by such slight increase of vacancies,[41] suggesting that the type-II band alignment is preserved in the heterodimers. Only remarkable change is an evolution of localized surface plasmon resonance in the $Cu_{31}S_{16}$ phase of heterodimer, compared to the $Cu_{1.94}S$ phase of CdS–$Cu_{1.94}S$ nanodisk. Therefore, we conclude that the dominant quenching process of exciton in the CdS–$Cu_{31}S_{16}$ heterodimer is ultrafast energy transfer to the localized surface plasmon rather than the electron transfer to the CdS phase. The efficient energy transfer from the excited CdS to localized surface plasmon of the $Cu_{31}S_{16}$ phase would also quench the PL from the CdS phase.

Conclusions

In conclusions, novel CdS–$Cu_{31}S_{16}$ heterodimers were synthesized by an in-situ seeded growth process. The monoclinic $Cu_{31}S_{16}$ phases selectively grew on the preformed hexagonal CdS (100) planes. It was revealed that the vacancy in the copper sulfide phase determines the carrier dynamics of the semiconductor–semiconductor heterodimers. The hole-induced localized surface plasmon in the $Cu_{31}S_{16}$ phases seems efficiently quench the photo-generated exciton even in a heterodimer. The combination of semiconductors in heterodimers should be carefully chosen taking the physics in NPs under the consideration for future optical device developments.

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Notes and references

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References

1 J. Hu, L.-S. Li, W. Yang, L. Manna, L.-W. Wang and A. P. Alivisatos, *Science*, 2001, **292**, 2060.

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2 Y. A. Yang, H. Wu, K. R. Williams and Y. C. Cao, *Angew. Chem. Int. Ed.*, 2005, **44**, 6712.
3 C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.*, 2000, **30**, 545.
4 A. P. Alivisatos, *J. Phys. Chem.*, 1996, **100**, 13226.
5 V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdate, H. J. Eisler and M. G. Bawendi, *Science*, 2000, **290**, 314.
6 M. Saruyama, M. Kanehara and T. Teranishi, *J. Am. Chem. Soc.*, 2010, **132**, 3280.
7 M. Kanehara, H. Arakawa, T. Honda, M. Saruyama and T. Teranishi, *Chem. Eur. J.*, 2012, **18**, 9230.
8 M. Eguchi, D. Mitsui, H.-L. Wu, R. Sato and T. Teranishi, *Langmuir*, 2012, **28**, 9021.
9 J. Henzie, M. Grünwald, A. Widmer-Cooper, P. L. Geissler and P. Yang, *Nat. Mater.*, 2012, **11**, 131.
10 K. Liu, Z. Nie, N. Zhao, W. Li, M. Rubinstein and E. Kumacheva, *Science*, 2010, **329**, 197.
11 P. D. Cozzoli, T. Pellegrino and L. Manna, *Chem. Soc. Rev.*, 2006, **35**, 1195.
12 T. Teranishi, M. Saruyama and M. Kanehara, *Nanoscale*, 2009, **1**, 225.
13 A. M. Smith and S. Nie, *Acc. Chem. Res.*, 2010, **43**, 190.
14 C. de Mello Donega, *Chem. Soc. Rev.*, 2011, **40**, 1512.
15 R. Bardhan, N. K. Grady, T. Ali and N. J. Halas, *ACS Nano*, 2010, **4**, 6169.
16 J. Zhang, Y. Tang, K. Lee and M. Ouyang, *Nature*, 2010, **466**, 91.
17 T. Mokari, E. Rothenberg, I. Popov, R. Costi and U. Banin, *Science*, 2004, **304**, 1787.
18 R. Costi, A. E. Saunders, E. Elmalem, A. Salant and U. Banin, *Nano Lett.*, 2008, **8**, 637.
19 E. Elmalem, A. E. Saunders, R. Costi, A. Salant and U. Banin, *Adv. Mater.*, 2008, **20**, 4312.
20 J. Yang, H. I. Elim, Q.-B. Zhang, J.-Y. Lee and W. Ji, *J. Am. Chem. Soc.*, 2006, **128**, 11921.
21 D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadtler and A. P. Alivisatos, *Nano Lett.*, 2007, **7**, 2951.
22 L. Carbone, C. Nobile, M. D. Giorgi, F. D. Sala, G. Morello, P. Pompa, M. Hytch, E. Snoeck, A. Fiore, I. R. Franchini, M. Nadasan, A. F. Silvestre, L. Chiodo, S. Kudera, R. Cingolani, R. Krahne and L. Manna, *Nano Lett.*, 2007, **7**, 2942.
23 J. E. Halpert, V. J. Porter and J. P. Zimmer and M. G. Bawendi, *J. Am. Chem. Soc.*, 2006, **128**, 12590.
24 H. McDaniel, J.-M. Zuo and M. Shim, *J. Am. Chem. Soc.*, 2010, **132**, 3286.
25 B. Koo and B. A. Korgel, *Nano Lett.*, 2008, **8**, 2490.
26 N. N. Hewa-Kasakarage, M. Kirsanova, A. Nemchinov, N. Schmall, P. Z. El-Khoury, A. N. Tarnovsky and M. Zamkov, *J. Am. Chem. Soc.*, 2009, **131**, 1328.
27 M. Saruyama, Y.-G. So, K. Kimoto, S. Taguchi, Y. Kanemitsu and T. Teranishi, *J. Am. Chem. Soc.*, 2011, **133**, 17598.
28 A. Rothwarf and A. M. Barnett, *IEEE Trans. Electron Devices*, 1977, **24**, 381.
29 J. B. Rivest, S. L. Swisher, L.-K. Fong, H. Zheng and A. P. Alivisatos, *ACS Nano*, 2011, **5**, 3811.
30 M. D. Regulacio, C. Ye, S. H. Lim, M. Bosman, L. Polavarapu, W. L. Koh, J. Zhang, Q.-H. Xu and M.-Y. Han, *J. Am. Chem. Soc.*, 2011, **133**, 2052.
31 I. Kriegel, C. Jiang, J. Rodríguez-Fernández, R. D. Schaller, D. V. Talapin, E. da Como and J. Feldmonn, *J. Am. Chem. Soc.*, 2012, **134**, 1583.
32 T. Teranishi, Y. Inoue, M. Nakaya, Y. Oumi and T. Sano, *J. Am. Chem. Soc.*, 2004, **126**, 9915.
33 T. Teranishi, M. Saruyama, M. Nakaya and M. Kanehara, *Angew. Chem. Int. Ed.*, 2007, **46**, 1713.
34 A. M. Smith, A. M. Mohs and S. Nie, *Nat. Nanotech.*, 2009, **4**, 56.
35 H. Fu, L.-W. Wang and A. Zunger, *Phys. Rev. B*, 1999, **59**, 5568.
36 H. Zhong and G. D. Scholes, *J. Am. Chem. Soc.*, 2009, **131**, 9170.
37 W. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart and P. N. Prasad, *Nano Lett.*, 2006, **6**, 875.
38 K. Kwon and M. Shim, *J. Am. Chem. Soc.*, 2005, **127**, 10269.
39 F. Shieh, A. E. Saunders and B. A. Korgel, *J. Phys. Chem. B*, 2005, **109**, 8538.
40 Y. Zhao, H. Pan, Y. Lou, X. Qiu, J.-J. Zhu and C. Burda, *J. Am. Chem. Soc.*, 2009, **131**, 4253.
41 P. Lukashev and W. R. L. Lambrecht, *Phys. Rev. B*, 2007, **76**, 195202.

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